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PROPERTIES AND MORPHOLOGY OF AMORPHOUS

HYDROCARBON BLOCK COPOLYMERS

by

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Because of the generally immiscible nature of long chain molecules, block copolymers often exhibit microphase separation. The morphologies of these heterogeneous materials are determined not only by the composition of the blocks but also by sample preparation conditions. The resulting microstructures exert a profound influence on the properties of the block copolymers. The purpose of this review is to discuss the more recent advances in the investigation of the relation between the morphology of block copolymers and their properties. First we shall discuss the thermodynamic conditions under which homogeneous block copolymers can be formed. These homogeneous systems are interesting because their underlying chain dynamics can be treated by the accepted molecular models. Viscoelastic relaxation times computed from these theories are in good agreement with experimental data. Next we present some examples of block copolymer morphologies, taken from the electron micrographs now available in the literature. Statistical theories capable of satisfactorily explaining the observed morphologies are then briefly discussed. Finally the elastic, viscoelastic and rheological properties of these materials are described. In all instances the dominant influence of the microdomain structure on these properties is demonstrated.

INTRODUCTION

During the past decade, there has been an upsurge of interest in studying the relation between morphology and properties of block co-polymers. The interest is generated mainly by the technological importance of these materials, e.g., their ability to form thermoplastic elastomers or impact resistant plastics. Although there are some block copolymers that are homogeneous, most of them show microphase separation. The type of structure depends on such variables as chemical composition, block configuration, solvent power, etc. Advances in characterization techniques such as electron microscopy and low angle x-ray scattering now render it possible to investigate their detailed morphologies. In this paper we shall review the morphological and property studies of both homogeneous and heterogeneous block copolymers, as well as the thermodynamic theories of microphase separation in these materials. The review is not intended to be exhaustive, rather it will focus on the more current works in the field. Further information is available in the recent research monographs (1-5) and review papers cited (6-10).

HOMOGENEOUS BLOCK COPOLYMERS

The thermodynamic criterion for the mixing of two or more systems is that the free energy of mixing must be negative. For polymeric systems, the entropy increases accompanying the mixing of long chain molecules are very small. Since the enthalpy of mixing is usually positive, it is therefore not too surprising that phase separations often occur in polymeric mixtures. The thermodynamic basis for micro-phase separation in block copolymers has been presented by Krause (11,12) and Meier (13). In the work of Krause, the enthalpy change on micro-phase separation is given by the Hildebrand-Van Laar-Scatchard expression (14):

$$\Delta H = -kT (V/V_z) v_A v_B \chi_{AB} (1-2/z) \qquad (1)$$

where V is the total volume of the mixture, V_z the volume of each lattice site, z is the coordination number, k is Boltzmann constant v_A and v_B are volume fractions of A and B blocks respectively, T is absolute temperature and χ_{AB} is the Flory-Huggins interaction parameter between A's and B's.

The entropy change accompanying microphase separation is ([12])

$$\Delta S/k = (v_A \ln v_A + v_B \ln v_B) - 2 (m-1)(\Delta S_d/k) + \ln (m-1) \qquad (2)$$

for each copolymer molecule. In eq. 2, m is the number of blocks in the block copolymer molecule. The entropy change due to the demixing from a homogeneous mixture to a phase separated system is given by the first term on the right hand side of eq. 2. The second term accounts for the entropy decrease due to the immobilization of the segments linking the A and B blocks (disorientation entropy). If the number of blocks in the copolymer is large (m>3), then it is necessary to recognize the fact that after the first block-linking segment has been placed on the interface, the possible number of sites available to the subsequent links is now constrained. The entropy change for this effect is given by the third term. Combining eqs. 1 and 2, the free energy change on microphase separation can be written. The critical interaction parameter can then be readily obtained by setting the free energy change to zero:

$$(\chi_{AB})_{cr} = \frac{zV_z}{(z-2)V_A n_A n_B} [-(v_A \ln v_A + v_B \ln v_B)$$

$$+ 2(m-1)(\Delta S_d/k) - \ln(m-1)] \qquad ((3)$$

where n_A and n_B are the numbers of A and B units in each copolymer molecule. Calculations on the basis of eq. 3 shows that the microphase separation becomes more difficult with increasing m. Values of critical interaction parameters computed for a mixture of homopolymers are much lower than those for the block copolymer with identical composition. Thus it is more difficult for microphase separation to take place when polymers are linked together via covalent bonds as block copolymers. Experimentally it has been found that although polyblends of polystyrene and poly(αmethyl styrene) tend to be heterogeneous, the corresponding block copolymers are often homogeneous (15-21).

Although there are very few homogeneous block copolymers availalbe, they are nevertheless of interest because their viscoelastic behavior can be studied within the existing theoretical framework to elucidate the molecular dynamics of block copolymers. The most accepted model is the molecular theory of polymer viscoelasticity proposed many years ago by Rouse (22), Bueche (23), and Zimm (24). The RBZ model divides the polymer molecule into N + 1 submolecules (beads) held together with N springs. The springs are stretched when the polymer coil is distrubed by a shear gradient. The spring constant is given by $3kT^3/b^2$, where b^2 is the average end-to-end distance of the submolecule. As the beads move through the medium, a viscous drag is exerted on them whose magnitude is given by a friction coefficient f. At equilibrium the viscous and elastic forces are equal to each other. A simplified form of the equation of motion can be written as follows:

$$\dot{\underline{x}} = \sigma \underline{Z} \, \underline{x} \tag{4}$$

where $\underline{x}$ and $\underline{x}$ are column vector of bead positions and bead velocities, $\underline{Z}$ is the nearest neighbor matrix and $\sigma = 3kT/b^2 f$.

In the case of block copolymers (25-29), Eq. 4 must be modified to take into account the fact that not all the beads are the same (as is the case for homopolymers). For a triblock copolymer such as poly(styrene-b-α-methyl styrene-b-α-methyl styrene), the equation of motion is (26):

$$\underline{\dot{x}} = -\sigma_s \, \underline{D}^{-1} \underline{Z} \, \underline{x} \tag{5}$$

where $\sigma_s = 3kT/b_s^2 f_s$, the subscripts s refer to the PS submolecule. The matrix $\underline{D}^{-1}$ is the inverse of

$$D = \begin{bmatrix} 1_1 & & & & \\ & \ddots & & \bigcirc & \\ & & \delta_A \delta_A & & \\ & & & \ddots & 1_1 \\ \bigcirc & & & & \ddots \end{bmatrix} \tag{6}$$

where $\delta_A = b_A^2 f_A / b_s^2 f_s$ and subscripts A refer to PαMS submolecules. Thus the elements in the diagonal of this matrix take into account the differences between the PS and PαMS submolecules.

The solution of the equation of motion yields the distribution of viscoelastic relaxation times. For ease of comparison with experimental data, maximum relaxation times for a number of block copolymers with different block configurations were computed (26). These are given in Table 1. Figure 1 shows the stress relaxation isotherms determined for two diblock copolymers of styrene and α-methylstyrene of two different molecular weight (21). These are shifted into smooth viscoelastic master curves (Figure 2). Their shift factors (Figure 3) are seen to follow the WLF equation closely, indicating the essential

homogeneity of the block copolymer samples. Similar experiments were also carried out for a number of triblock copolymers of styrene and α-methylstyrene (19). Maximum relaxation times were determined from the master curves by Procedure X of Tobolsky and Murakami (30). Table 2 shows that the agreement is satisfactory between the calculated and experimental values (10).

MORPHOLOGY OF HETEROPHASE BLOCK COPOLYMERS

Five fundamental domain structures are possible for block copolymers consisting of two types of blocks. Generally lamellar structures will form at compositions with approximately equal proportions of the two components. As the proportion of one component increases at the expense of the other, cylindrical morphologies will result. The matrix phase will be composed of the component in greater abundance. As the proportion of one component continues to increase, eventually the morphology of sperical domains of minor component embedded in the matrix of the other component appears. These structures have been observed for diblock copolymers of isoprene and styrene cast from toluene (31). Their electron micrographs are shown in Figure 4. The dark regions belong to the polyisoprene (PIP) phase which was selectively stained by OsO_4. The domain structure of the 20/80 styrene/isoprene block copolymer (Figure 4a) shows tiny spheres of polystyrene (PS) blocks dispersed in a matrix of polyisoprene. Electron micrographs of 40/60 and 50/50 compositions (Figure 4b and 4c) appear as alternating stripes which are actually profiles of the three dimensional lamellar structures. For the 60/40 block copolymer, cylindrical domains of the isoprene component in PS matrix can be observed (Figure 4d). The dark dots represent ends of the cylindrical rods.

The progressive changes in morphology with changing compositions can also be achieved by adding homopolymers to the block copolymer (32-35). The added homopolymer is solubilized into the corresponding domains in the block copolymer if the molecular weight of the added homopolymer is equal to or less than that of the corresponding block in the copolymer. Figure 5a shows the electron photomicrograph of a triblock copolymer of styrene-butadiene-styrene (SBS) cast from a mixed solvent of tetrahydrofuran/methyl ethyl ketone. Incorporation of a low molecular weight polystyrene (PS) in the block copolymer enlarged the PS domains (light regions), as seen in Figure 5b. However, if the added PS has a molecular weight that is greater than that in SBS, then separate domains of pure PS appears (Figure 5c).

Under appropriate conditions it is possible to observe long range order in block copolymers, e.g., if samples are prepared by melt extrusion, thermal annealing or slow rate of casting (36-42). An example for a styrene-butadiene block copolymer containing 68% styrene is shown in Figure 6. These structures are often referred to as "macrolattice." In some instances imperfections in the long range order may appear as "grain boundaries" normally found in metallic systems. These electron microscopic observaitons are supported by small angle x-ray scattering (SAXS) and optical light scattering studies (39-42).

THEORIES OF MICRODOMAIN FORMATION

The basic driving force for microdomain formation in block copolymers is the reduction in the positive surface free energy of the system resulting from the increase of the domain size. This domain size increase gives rise to a decrease in the volume fraction of interfacial region in which junction points of the copolymers must be distributed. In addition, configurations of the block chains must also

change in order to even up the density deficiency in the interior of the domains.

A number of statistical thermodynamic theories for the domains formation in block and graft copolymers have been formulated on the basis of this idea. The pioneering work in this area was done by Meier (43). In his original work, however, he assumed that the boundary between the two phases is sharp. Leary and Williams (43,44), were the first to recognize that the interphase must be diffuse and has a finite thickness. Kawai and coworkers (31) treated the problem from the point of view of micelle formation. As the solvent evaporates from a block copolymer solution, a critical micelle concentration is reached. At this point, the domains are formed and are assumed to undergo no further change with continued solvent evaporation. Minimum free energies for an AB-type block copolymer were computed this way.

Helfand (45,46), used a mean field approach to treat the problem of microdomain formation (Figure 7). For a diblock copolymer with a high degree of polymerization, the following free energy expression can be written (46):

$$\frac{G}{NkT} = (\frac{2\gamma}{kT}) \ (\frac{x_A}{\rho_A} + \frac{x_B}{\rho_B}) \ (\frac{1}{d}) + \log \ (\frac{d}{2a_J})$$

$$+ \ 0.141 \ d^{5/2} \left\{ \frac{(x_A^{1/2}/b_A\rho_A)^{5/2} + (x_B^{1/2}/b_B\rho_B)^{5/2}}{[(x_A/\rho_A) + (x_B/\rho_B)]^{5/2}} \right\}$$

$$- \ \frac{\alpha(x_A/\rho_A)(x_B/\rho_B)}{(x_A/\rho_A) + (x_B/\rho_B)} \tag{7}$$

The first term on the right hand side of eq. 7 accounts for the energy of mixing at the interphase, and the entropy loss resulting from the

fact that an A-chain (or B-chain) which has penetrated into the B-phase (A-phase) must turn back. In this term, γ is the interfacial tension, x is the degree of polymerization and ρ is the density of pure A or B. In addition, the interfacial term must decrease with increasing domain size, which goes as 1/d where d is the domain repeat distance. The second term of this equation is attributable to the necessity of the segment linking A and B blocks being confined to the interphase. It is proportional to the logarithm of the ratio of the volume available to the link in a mixed homogeneous state to that in the microdomains. The width of the interfacial region is given by a_J, and is generally of the order of nanometers. Another consequence of the confinement of the link to the interphase is the density deficiency in the interior of the domain. The system tends to statistically reduce the conformations which lead to the inhomogeneous density, and favor the rarer conformations in the center of the domain. The loss of conformational entropy will increase with increasing size of the domain, which is represented by the third term of eq. 7. The symbol b in this term is the statistical length of a monomer unit. The last term in the equation is independent of domain size, and fixes the standard state of the system as that of a homogeneous mixed state. Here α is a measure of the repulsion between A and B blocks. By minimizing eq. 7, d can be calculated. Table 2 shows that the computed values of d's are in satisfactory agreement with available experimental data for a number block copolymers of styrene and butadiene.

In their statistical model for microphase separation of block copolymers, Leary and Williams (43) proposed the concept of a separation temperature T_s. It is defined as the temperature at which a first

order transition occurs when the domain structure is at equilibrium with a homogeneous melt, i.e.,

$$\Delta G = \Delta H - T\Delta S = 0 \qquad (8)$$

or

$$T_s = (\Delta H/\Delta S)_{demix} \qquad (9)$$

Value of the separation temperature for a series of poly(styrene-b-butadiene-b-styrene) were determined by light transmission, calorimetry, electron microscope observations (44). A comparison between these experimental and calculated values of T_s is given in Table 4. Further evidence for the existence of such "structured-unstructured" transitions through rheological measurements will be given in a later section.

ELASTICITY OF HETEROPHASE BLOCK COPOLYMERS

The stress-strain behavior of heterogeneous block copolymers depends on their chemical composition. Those consisting of a soft rubbery component and a hard glassy component may either be rubber-like or plastic-like. In triblock copolymers where the former is the major component, the stress-strain curves would exhibit high elasticity up to nearly 1,000% before fracture. The rubber-like elasticity arises from the fact that the plastic domains "anchor" the rubbery network chains as pseudocrosslinks. In addition, these domains also have the reinforcing effect of fillers (47). Leonard (48) derived an equation of state for such systems:

$$f = (NRT/v_r^{1/3}L_o) \ (1.0 + 2.5 \ v_p + 14.1 \ v_p^2 \ (\lambda - 1/\lambda^2) \qquad (10)$$

where f is the elastic force, R is the ideal gas constant, T is the absolute temperature, L_o is the unstretched length, v_r and v_p are volume fractions of the rubbery and plastic components respectively, N is the number of rubber chains anchored between 2N domains, and λ is the elongation ratio. The theory was derived from entropy considerations of the heterogeneous system, although the resulting equation is identical to the classical statistical theory of rubber elasticity.

Block copolymers in which the plastic component is sufficiently abundant to form continuous regions may be regarded as microcomposite materials. The dispersed domains in these materials are microscopic rather than macroscopic in dimensions. A number of existing theories for the elasticity of composites has been successfully applied to calculate the elastic moduli of these materials. Takayanagi (49) and Kawai (50) and their coworkers were among the first to treat the elastic moduli as composites. They chose an equivalent model to represent composites, using the degree of mixing (λ) of the dispersoids and the composition (ϕ) of the dispersoids and matrix as independent variables. Perfect material contact between the phases is assumed. When the equivalent model is stretched, the elastic force may be borne by the matrix alone or by both the matrix and the dispersed phases. The modulus of the equivalent model can be calculated by either the Series Model or the Parallel Model. For the Series Model, the modulus of the composite is

$$M = \lambda \left[\frac{\phi}{M_d} + \frac{(1-\phi)}{M_m} \right]^{-1} + (1-\lambda) M_m \tag{11}$$

and for the Parallel Model,

$$M = \left[\frac{\phi'}{\lambda' M_d + (1-\lambda') M_m} + \frac{(1-\phi')}{M_m} \right]^{-1} \tag{12}$$

where subscripts d and m refer to dispersed and matrix phases re-
spectively, v_s are the volume fractions of the two phases, and $\lambda\phi = v_d$.
The unprimed λ and ϕ refer to the Series Model, while the primed ones
to Parallel Model. The two models are in fact equivalent, if
$\lambda' = 1 - v_d - \phi$ (51,52). Eqs. 11 and 12 have been employed by a number
of authors (51-53), to compare with experimentally determined elastic
moduli of heterophase block copolymers. However, the Series - Parallel
Model is only valid for soft dispersoids in hard matrix in concentration
ranges where geometry of the dispersed phase is not important. For the
inverse case of hard dispersoids in soft matrix the moduli data cannot
be adequately predicted by the model. Halpin (54) and Nielsen (55,56)
proposed a more general equation that covers the complete composition
range. But as the composition of the block copolymer changes a phase
inversion may occur at a certain point. For such a situation, the use of
some empirical mixing rules is necessary. Recently, Faucher (57) pointed
out that by using the "polyaggregate" model of Kerner (58), it is not nec-
essary to postulate the existence of the matrix phase. In fact the model
implies the equivalence of the two phases. Since neither one can be re-
garded as the matrix for the other, the difficulty of treating the phase
inversion is circumvented. The resulting equations are lengthy, but
the predictions appear to agree well with literature data.

For plastic-like heterophase block copolymers, the stress-strain
behavior is strongly dependent on morphology. Kawai and coworkers (59)
found that for a 50/50 diblock copolymer of styrene-isoprene cast from
a mixed solvent system of toluene and methyl ethyl ketone, the stress-
strain curve shows regions of yielding and drawing. Transmission
electron micrographs show that there is extensive elongation of the
plastic domains in the region of drawing. These authors hypothesized

that these morphological changes may be due to heat transformed from the strain energy, thereby causing the flow to take place upon stretching.

Under appropriate conditions of sample preparation, the phenomena of "strain induced plastic-rubber transition" can be observed. For block copolymers exhibiting yielding and drawing region in the first stress-strain cycle, there is usually considerable strain-softening in the second and subsequent deformation (60-63). The drawing process occurs when the narrowing of the crosssectional area of the sample suddenly appears at one point in the sample, and subsequently propagates until the entire sample is transformed. Such phenomena are similar to that in conventional plastics, except that in this instance the necked regions is not plastic but rubbery. After the necking process has propagated throughout, the sample which was initially a plastic has now become a rubber. The electron micrographs show that there is extensive disruption of the continuous polystyrene domains in the stretched sample. If the sample is annealed at elevated temperature, then the sample returns to the plastic state (63). These morphological changes can also be observed by small angle x-ray scattering (SAXS) in Figure 8. The unstretched sample of a poly(styrene-b-butadiene-b-styrene) blended with 20% polystyrene shows a rather sharp peak, but becomes broadened upon stretching. The scattering curve for the annealed sample, however, is more similar to that of the unstretched sample, indicating a partial restoration of the original morphology (64).

The mechanical properties of a macrolattice of SBS has been investigated (65). The sample consists of a hexagonal array of polystyrene cylinders embedded in the polybutadiene matrix. The stress-strain curves of the macrolattice show a decisive anisotropy. The moduli data were found to be in excellent agreement with the Takayanagi-

Kawai model if the longitudinal sample is represented by parallel coupling and the transverse sample by series coupling.

VISCOELASTICITY OF HETEROPHASE BLOCK COPOLYMERS

In an earlier section, we have shown that the viscoelastic behavior of homogeneous block copolymers can be treated by the modified Rouse-Bueche-Zimm model. In addition, the Time Temperature Superposition Principle has also been found to be valid for these systems. However, if the block copolymer shows microphase separation, these conclusions no longer apply. The basic tenet of the Time Temperature Superposition Principle is valid only if all of the relaxation mechanisms are affected by temperature in the same manner. Materials obeying this Principle are said to be thermorheologically simple. In other words, relaxation times at one temperature are related to the corresponding relaxation times at a reference temperature by a constant ratio (the shift factor). For heterogeneous systems, the constituent polymers exist in separate phases and must undergo relaxation processes individually. Such hetero-geneous block copolymers therefore do not satisfy the said stipulation, and should be considered thermorheologically complex (66-69). Their master curves are in fact different in shape at different temperatures be-cause the relaxation times of the two different phases are affected by temperature differently. However, the experimentally accessible range (which Fesko and Tschoegl (66) call "the experimental window") is small. Within this window the neighboring isotherms appear to be superposable by simple horizontal shifting along the logarithmic time axis, but the result of such shifting would give rise to an erroneous master curve. A useful way to represent the viscoelasticity of heterogeneous systems is the contour plot, an example for which is shown in Figure 9. Such a plot shows simultaneously how a given viscoelastic parameter, in this

case the dynamic loss compliance, depends on both the frequency
(or time) and temperature (70).

The effect of morphology on the viscoelasticity of block copolymers
has been investigated (71,72). The most important factor appears to be
the connectivity of domains. If the sample was cast from a solvent
which results in extensive interconnections among the hard domains (for
instance the glassy PS domains in SBS), then the modulus in the region
(above the T_g of PS) will be relatively high. On the other hand, if
the hard domains are dispersed in a soft matrix (the rubbery PB domains),
then the moduli in the same region will be lower for the same sample
(71). In addition, the ratio of storage moduli (E'/G') in tensile and
shear modes was found to be nearly three for the PB-continuous SBS,
which is as expected for elastomers. However, the ratio for the same
sample which was cast from solvents that render them PS-continuous is
now greater by an order of magnitude (72). The anomalously high value
is attributed to the anisotropic PS domain connectivity in the form of
long fibrils or lamellae.

RHEOLOGY OF HETEROGENEOUS BLOCK COPOLYMER MELTS

Because the existence of domain structure in heterogeneous block
copolymers persists even in the molten state, their rheological behavior
is rather unique when compared with homogeneous polymer melts. Holden
et. al. (47) first noted the peculiar characteristics in the steady
shear behavior of the SBS block copolymer melts. For certain composi-
tion of styrene and butadiene, no limiting Newtonian viscosity was found
at low shear rates. For some of the others, there exist two distinct
viscosity vs. shear rate relationships (Fig.10). Arnold and Meier (73)
carried out the experiments in oscillatory shear, and found the same

anomaly. In addition, these authors found that the viscosities obtained were much higher than that of either homopolymer of the same molecular weight as the block copolymer. The absence of a Newtonian viscosity was explained in terms of a fluid domain structure in the melt that was progressively disrupted, causing the viscosity to decrease markedly with increasing shear rate. The high viscosity is attributed to the additional work needed to overcome the thermodynamic resistance to the mixing process for the different block species to flow past each other.

Kraus et al. (74,75) studied the steady flow and oscillatory flow behavior of linear triblocks of S-B-S and B-S-B, and radial block copolymers of the type $(B-S-)_3$, $(S-B-)_3$ and $(S-B-)_4$. For block copolymers of the same molecular weight and composition, those with end blocks of PS always have higher viscosities. However, when compared with linear corresponding linear block copolymers, the viscosities of the radial block copolymers are generally lower.

More recently, it has been demonstrated that many of the unusual rheological behavior of block copolymers will disappear when the measurements were carried out at temperatures higher than the separation temperature proposed by Leary and Williams (43). Figure 11 shows that for a bulk SBS block copolymers with a composition of 7-43-7 $(x10^3)$, the transition occurs around 145°C (especially clear at low frequencies) (76,77). These data are consistent with those of Pico and Williams on plasticized block copolymers (78).

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TABLE 1. Block Configurations and Maximum Retardation Times of Block Copolymers (26)

POLYMER	BLOCK CONFIGURATION	Log τ_{max}*	
		10% A	50% A
I. Diblock Copolymer	A_xB_y	-0.42	0.65
II. Triblock copolymers	(a) $A_xB_yA_x$	0.64	1.22
	(b) $B_xA_yB_x$	0.62	0.65
III. Alternating (Segmented) Block Copolymers	(a) $A_xB_xA_xB_x\cdots$	0.26	0.97
	(b) $A_xB_yA_xB_y\cdots$	---	0.97
IV. Multiblock Copolymers	(a) $B_xA_yB_z$	0.60	0.65
	(b) $B_xA_yB_zA_yB_x$	0.34	1.01

*Computed for $\partial_A = 185$.

Table 2. Maximum Viscoelastic Relaxation Times for Block Copolymers
of Styrene and α-Methylstyrene

Sample	Wt% αMS	log (τ_m/τ_m°)		Ref.
		Expt'l	Cal'd	
SAS	5	0.50	0.50	19
	17	0.59	0.55	19
	34	0.01	1.10	19
	42	0.89	1.50	19
	65	1.76	1.90	19
ASA	73	2.26	2.30	19
AS	50	1.75	1.75	21

Table 3. Microdomain Repeat Distances in Block Copolymers of
         Styrene and Butadiene (46)

Polymer	Mol. Wt. (kg/mole)	d_{exp} (nm)	d_{calc} (nm)
I. Lamellar Morphology			
S-B	32-48	44.5	51
	35.5-54.5	49	55
	71-46	74	63
	48.9-32.4	46	49
B-S-B	19.4-72-19.4	40	38
	24-72-24	44	41
	37.5-72-37.5	48	48
	73-72-73	66	64
S-B-S	14.1-27.9-14.1	27-30	24
	17-68-17	30	38
	14-30-14	26	25
II. Spherical Morphology			
S-B	7.2-33	8.6	8.4
	8-40	10.7	9.3
	11-47	10.8	11.1
	12-147	11.2	11.6
	12-163	10.9	11.4
	13-59	12.8	12.4
	15-32	11.2	14.3
	15-83	12.2	13.8
	13-75-13	13.5	13.1
	10-71-10	10	10.7
	7-35-7	9.3	8.5
	14-63-14	11.6	13.5
	21-98-21	17.0	18.1
	120-660-120	21	58

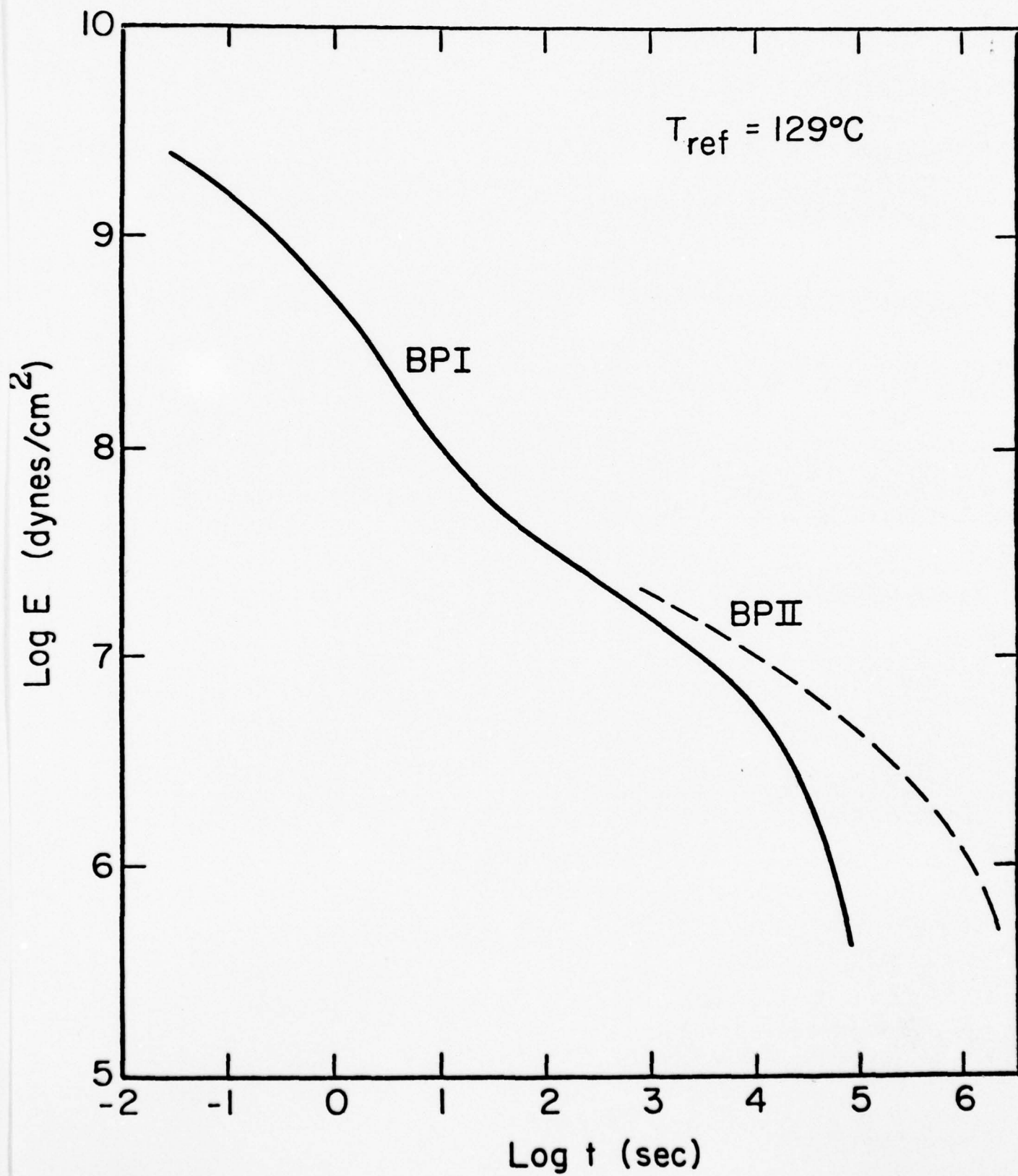Table 4. Separation Temperatures in Triblock Copolymers of Styrene and Butadiene (44)

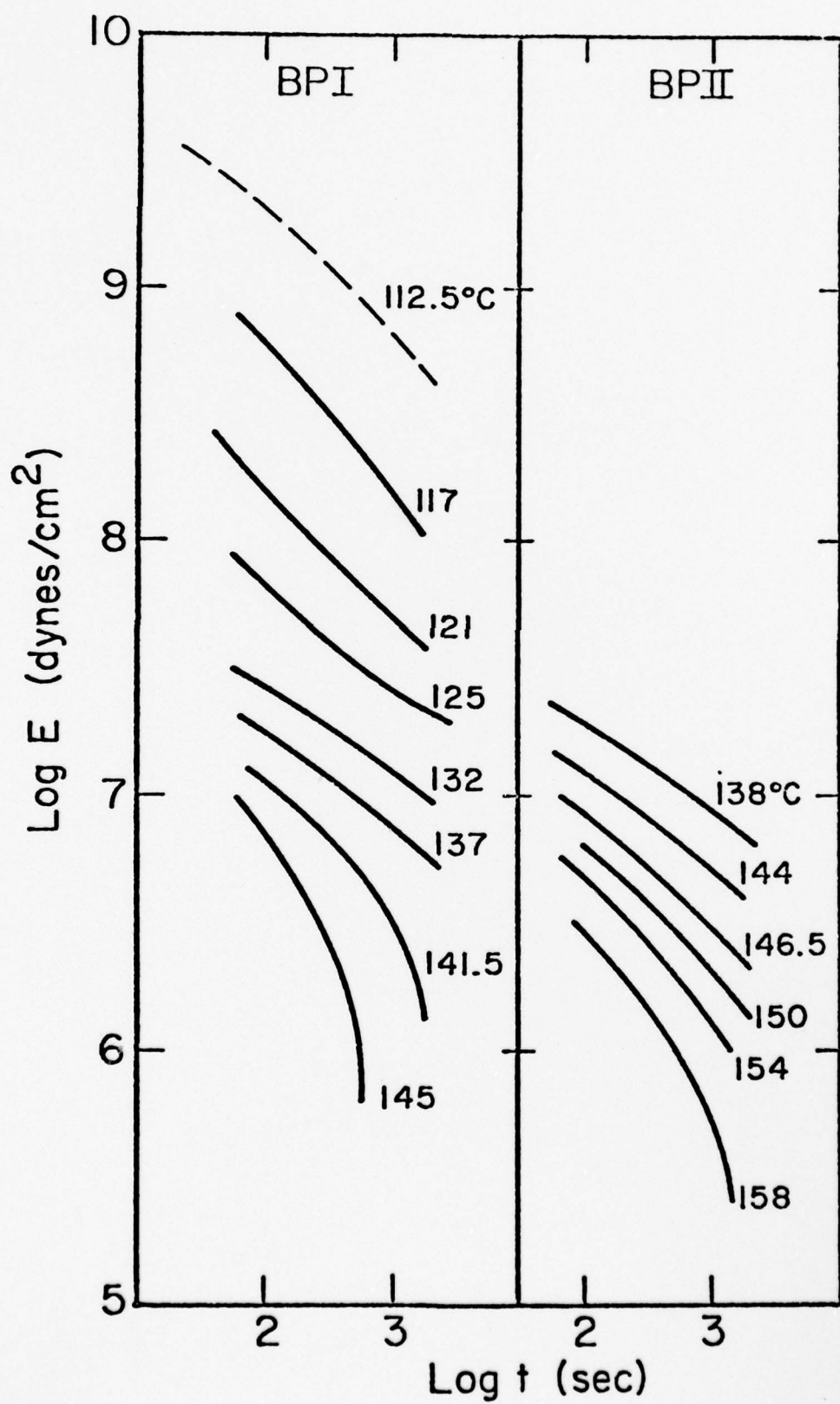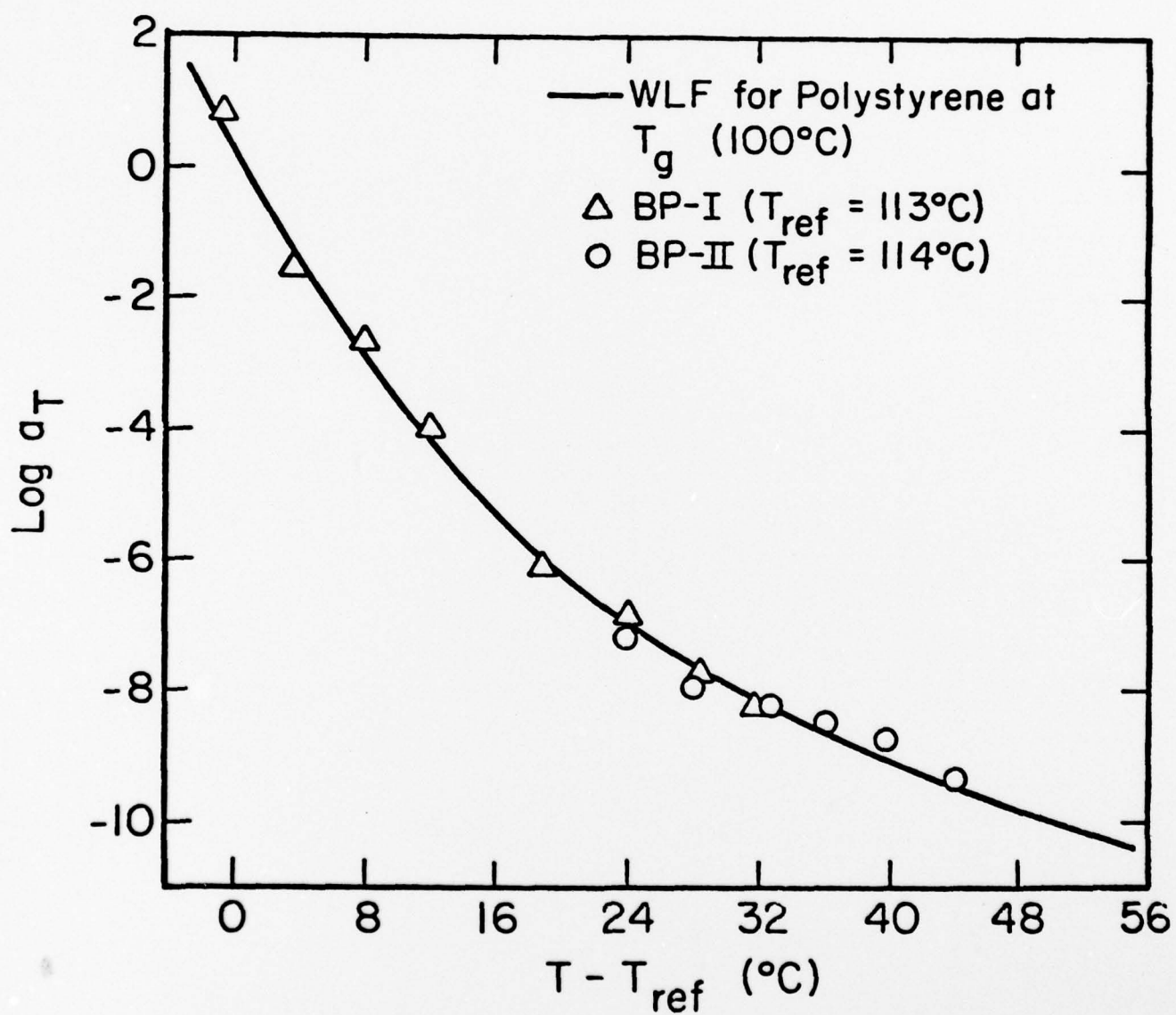| Polymer	Molecular weight x 10⁻³		Volume fraction styrene, ϕ_s	T_s (°K)		Method
	$M_s - M_B - M_s$	$\bar{M}_n$		Model	Observed	
Kraton 1101	12.5-75-12.5	100	0.245	590	583-593	Light transmission
					>343	Calorimetry
Kraton 1102	5.4-32.3-5.4	43	0.245	265	373-423	Light transmission
	9.4-56.2-9.4	75	0.245	430	>340	Calorimetry
TR-41-1647	7-36-6	49	0.25	298	<310	Calorimetry
TR-41-1648	16-78-16	112	0.275	735	>600	Light transmission
					>347	Calorimetry
TR-41-1649	14-30-14	58	0.463	515	<530	Electron microscope
					>500	Calorimetry
					573-598	Light transmission

CAPTIONS FOR FIGURES

Figure 1: Stress relaxation isotherms for two samples and of poly(styrene-b-α-methylstyrene), BPI=$\bar{M}_w$=0.8x10^5;BPII=$\bar{M}_w$=1.5x10^5. Solid curves: tensile data; broken curve: flexural data, (21).

Figure 2: Viscoelastic master curves of poly(styrene-b-α-methylstyrene). Solid curve: sample BPI, broken curve: sample BPII, (21).

Figure 3: Viscoelastic shift factor data for samples BPI (triangles) and BPII (circles) of poly(styrene-b-α-methylstyrene). The solid curve was calculated from the WLF equation, (21).

Figure 4: Electron micrographs of diblock copolymers of styrene and isoprene cast from toluene, and microtomed normal to the surface as indicated (31). (Reproduced by permission of Kyoto Univ., Japan).

Figure 5: Electron micrographs of triblock copolymers of styrene and butadiene. (a) As cast from tetrahydrofuran/methyl ethyl ketone;
(b) Cast from the same solvent with 20% polystyrene ($\bar{M}_n$=3,000);
(c) Cast from the same solvent with 20% polystyrene ($\bar{M}_n$=30,000).

Figure 6: Electron micrograph of diblock copolymer of styrene and butadiene cast from xylene (courtesy of Dr. M. Hoffman).

Figure 7: Schematic diagram of a lamellar microdomain structure in block copolymers (46).

Figure 8: Small angle x-ray scattering (SAXS) data for poly(styrene-b-butadiene-b-styrene) blended with 20% polystyrene and cast from tetrahydrofuran/methyl ethyl ketone. (After ref. 64).

Figure 9: Contour plot (70) of dynamic loss compliance as a function of frequency and temperature for poly(styrene-b-butadiene-styrene). (Reproduced by persmission of John Wiley and Sons).

Figure 10: Shear viscosity as a function steady state shear rate
for poly(styrene-b-butadiene-b-styrene) at 150°C. (After ref. 47).

Figure 11: Dynamic shear viscosity as a function of temperature
for poly(styrene-b-butadiene-b-styrene) at various angular frequencies
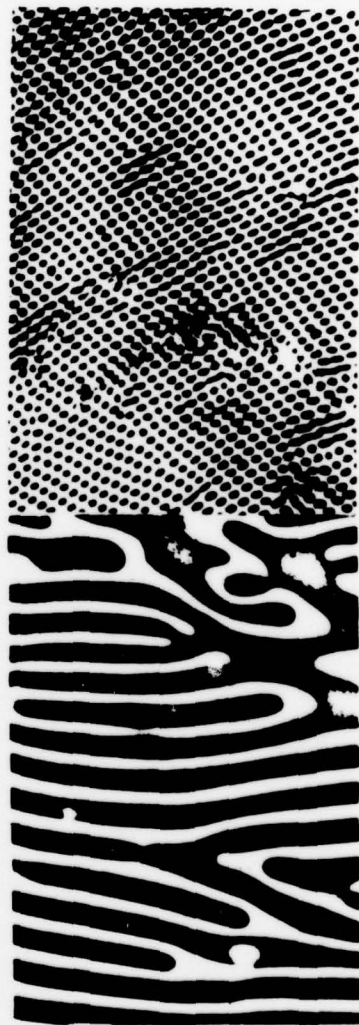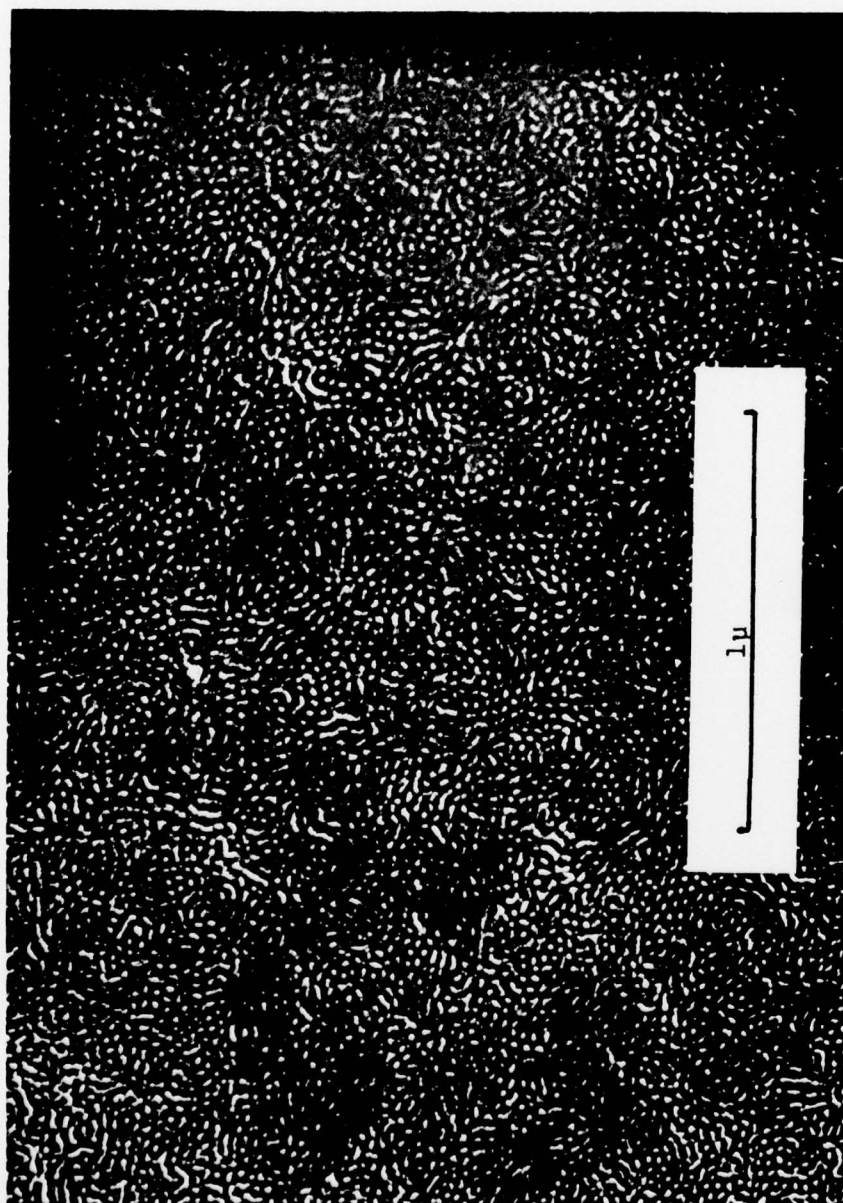(77). (Reproduced by permission of John Wiley and Sons).
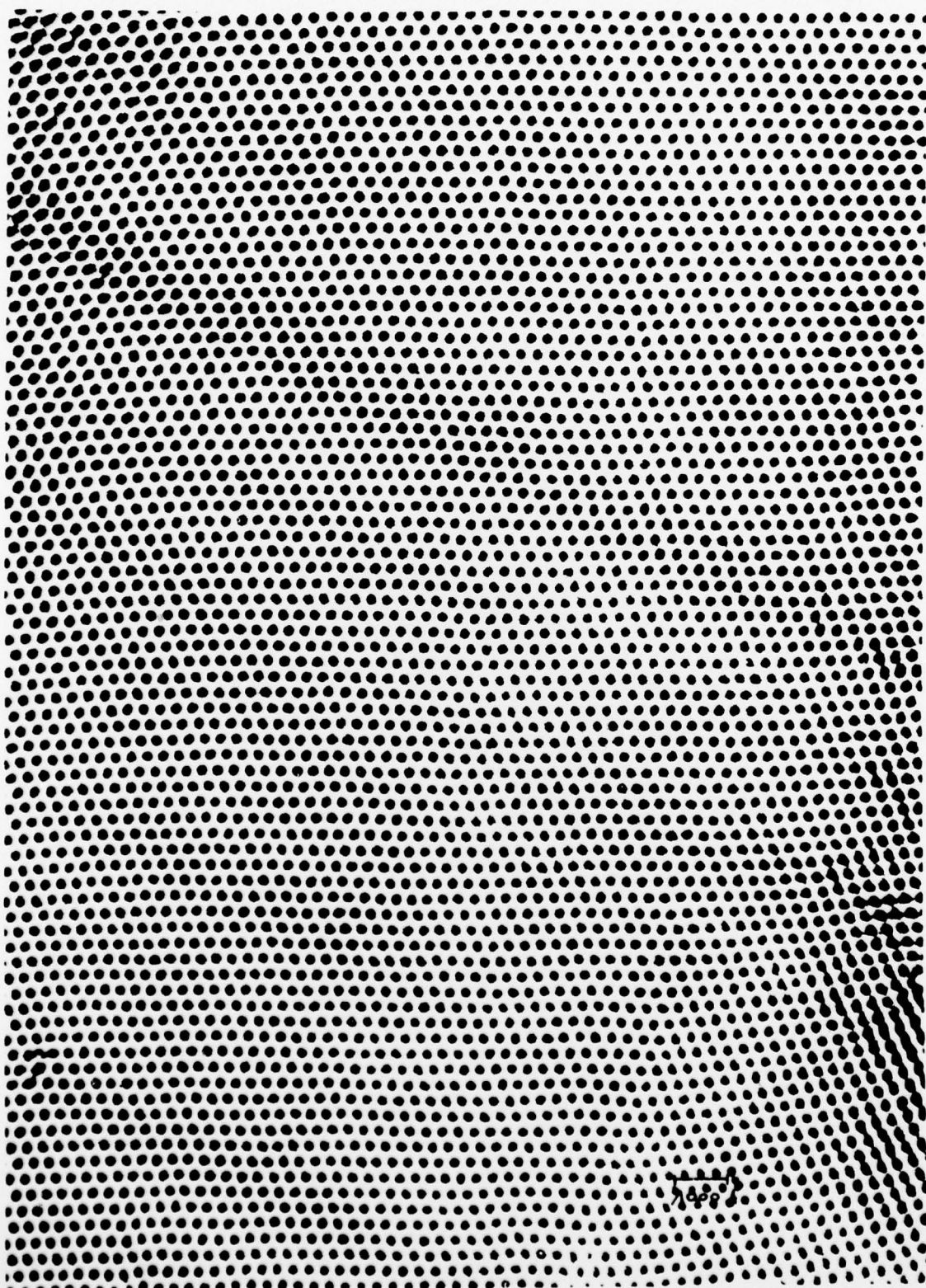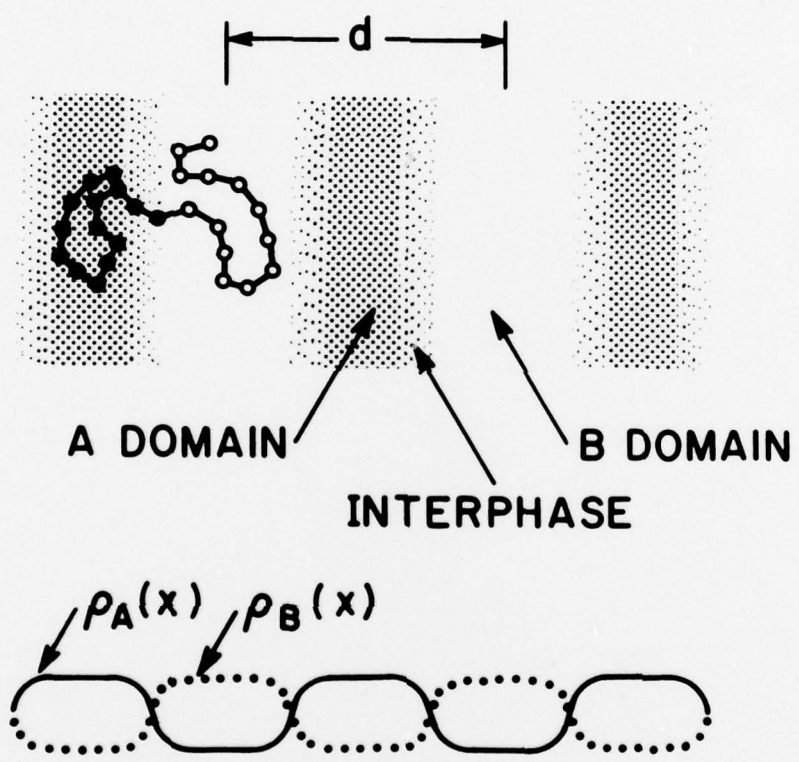
(a) (SI-1, 20/80 Sty-Isop)

(b) (SI-2, 40/60 Sty-Isop)
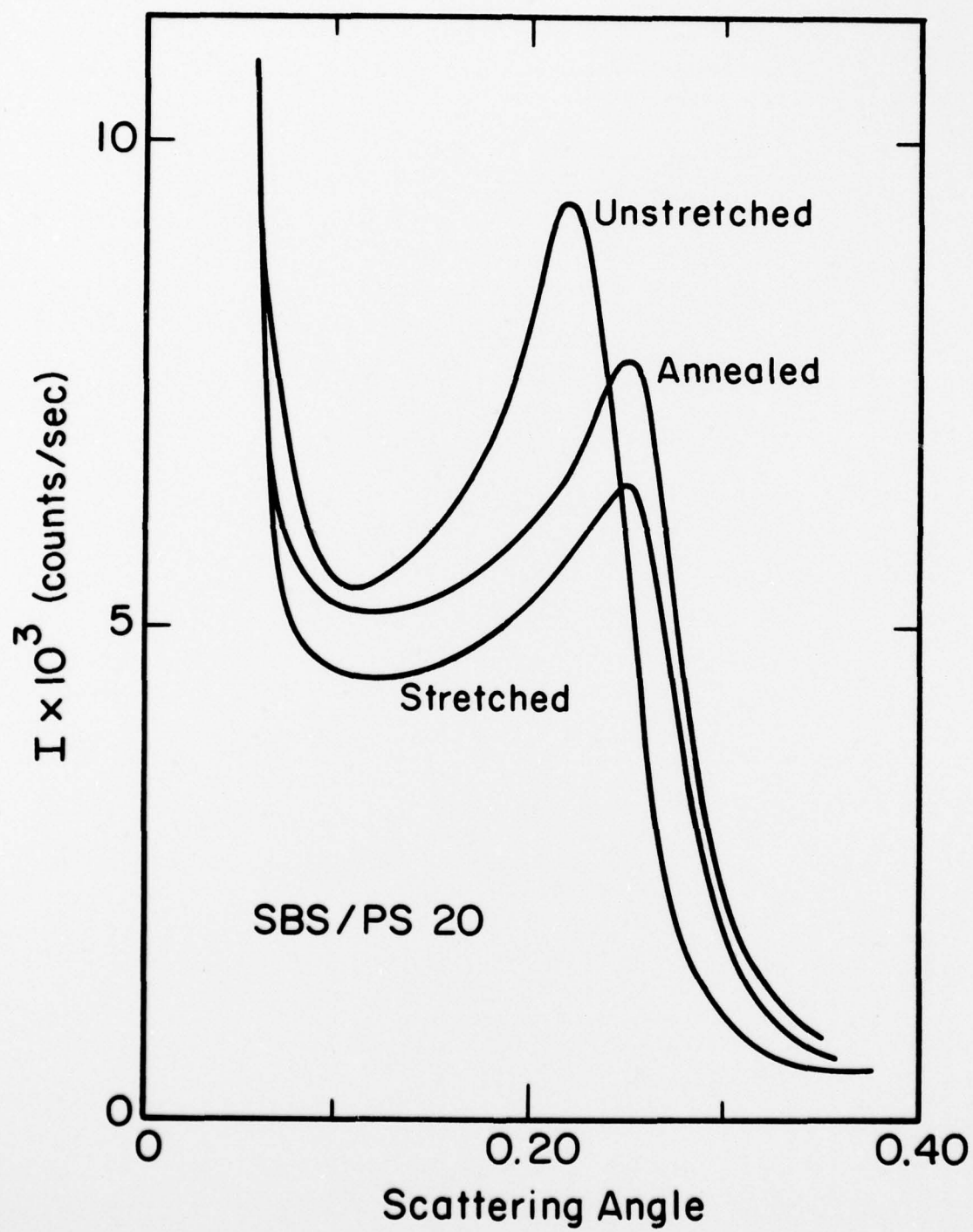
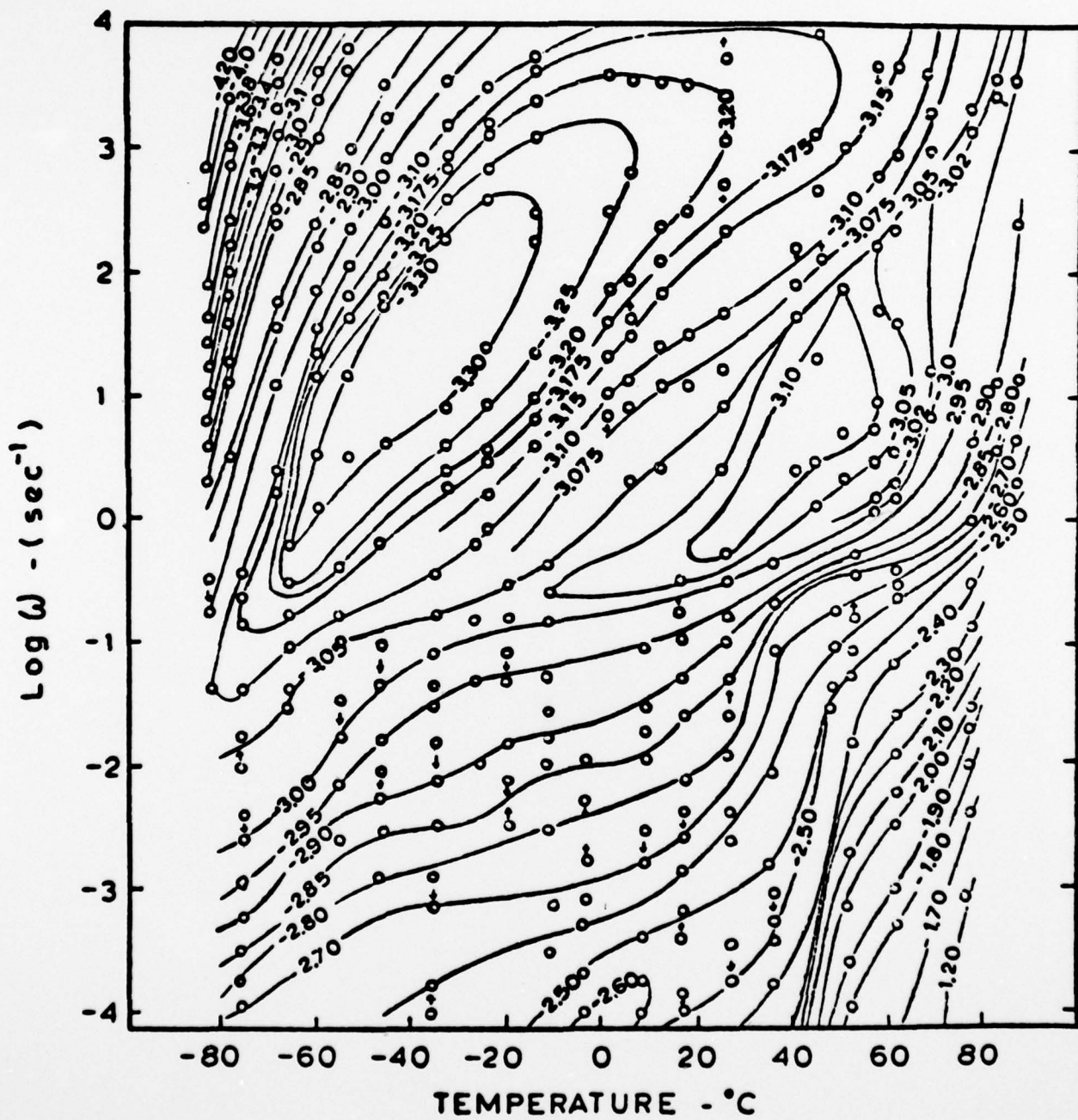(c) (SI-3, 50/50 Sty-Isop)

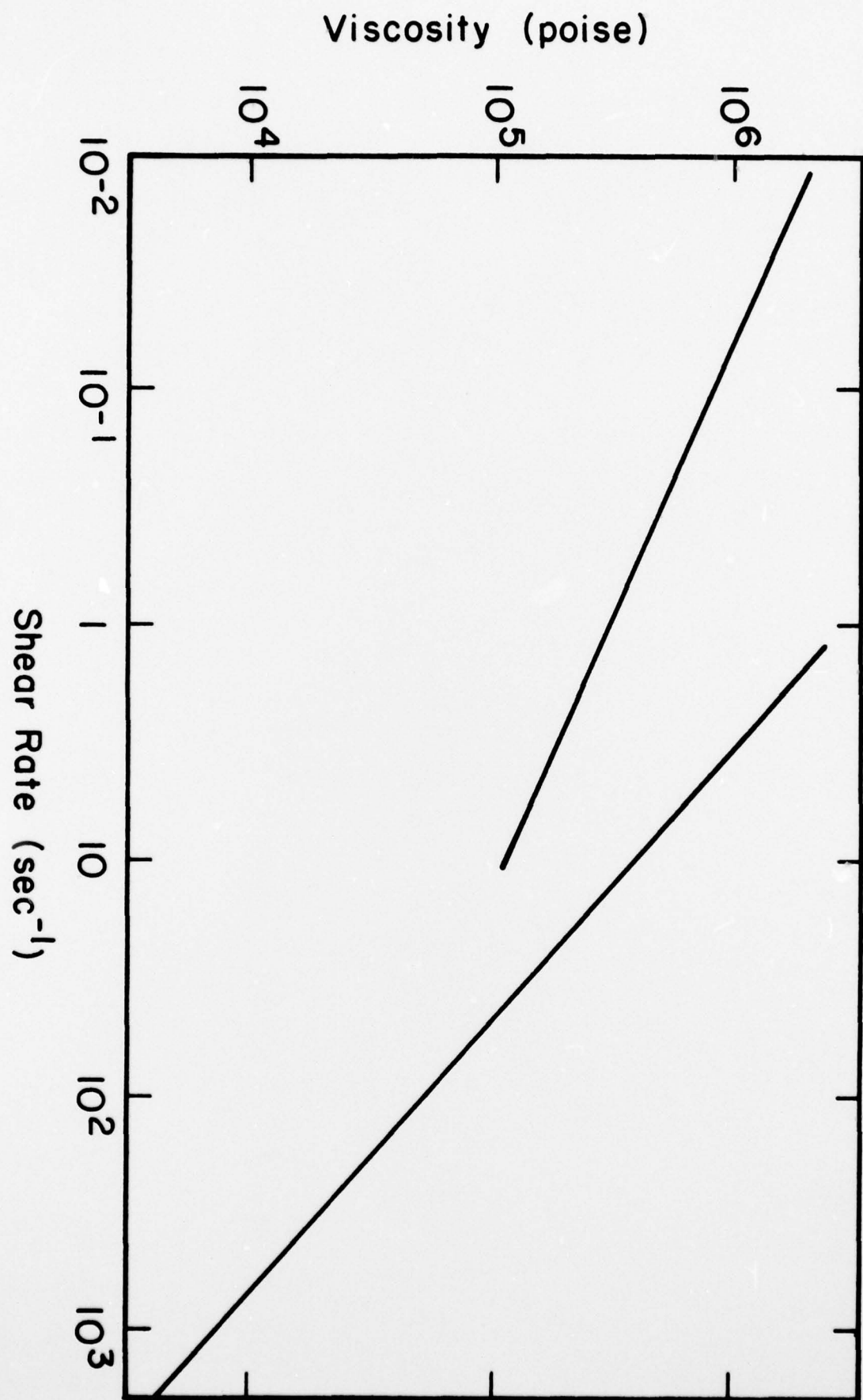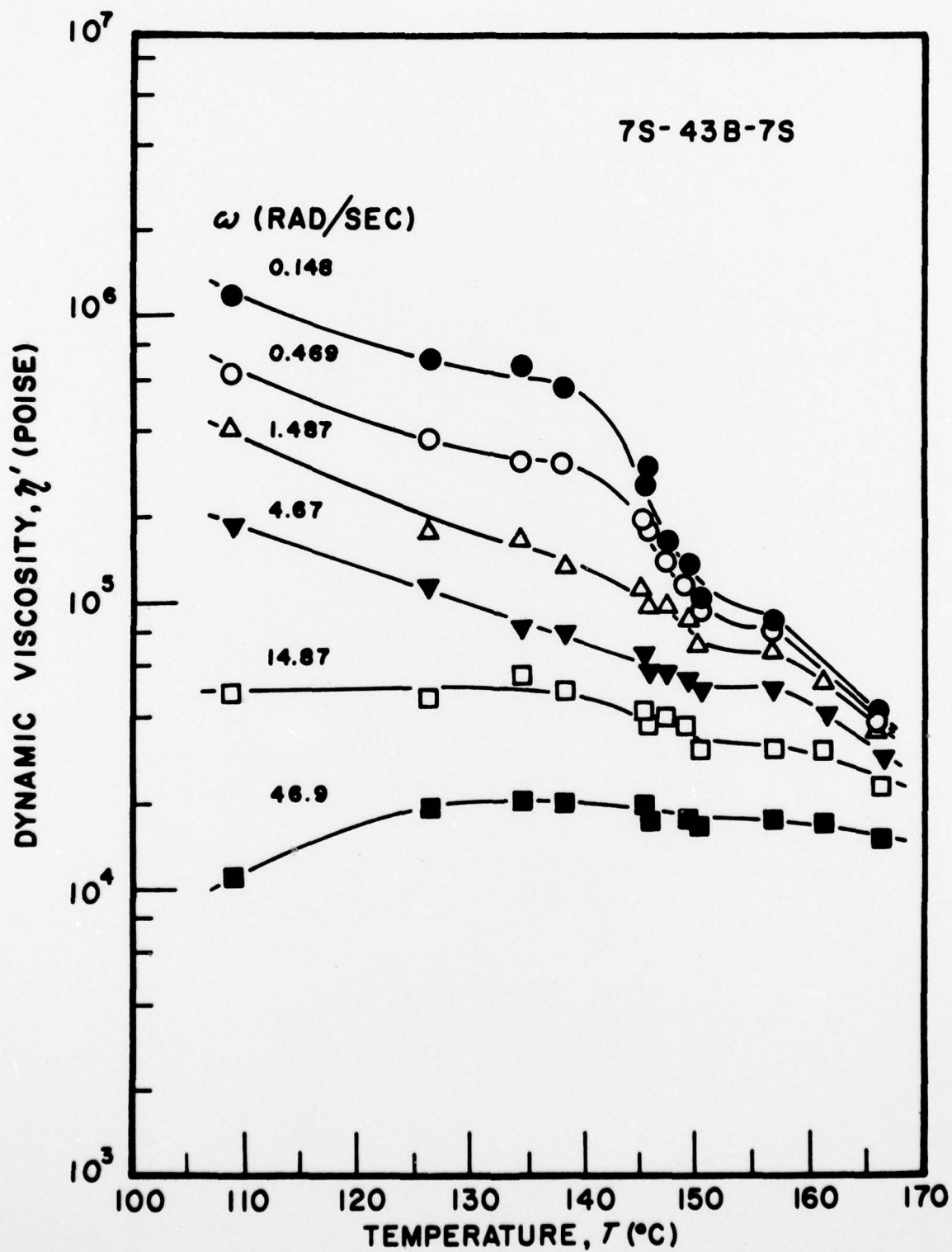(d) (SI-4, 60/40 Sty-Isop)

1μ

1 μ

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